# The Surface Science—Materials Research & Development Group
# and Sorbent/Catalyst Development Group

## FY01 TECHNICAL PROGRESS REPORT

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**DESCRIPTION:** The role of the Surface Science Team is to employ the techniques of surface science and catalysis to address current and emerging technical issues important and relevant to the division and office mission and role. Most of the research in the team is focussed on developing sorbents and catalysts to remove pollutants and greenhouse gases from fuel gas streams.

For FY2001, the Surface Science Team was involved in three major projects: sorbent development (hot/warm gas desulfurization), characterization of high temperature membranes utilized in hydrogen separation, and development of sorbents for carbon dioxide capture.

**RESEARCH OBJECTIVES:**

**1. Sorbent Development**

a) Development of a fluid/transport bed reactor sorbent

Development of a suitable regenerable sorbent is one of the major barrier issues in the gas cleanup program for IGCC systems. NETL researchers have developed a promising regenerable sorbent known as RVS-1 (formerly known as METC10) for removal of hydrogen sulfide from the gas streams. The moving bed version of this sorbent was the only sorbent that exceeded all the performance criteria for the TECO Clean Coal Project. This sorbent is operational at a temperature range of 260 -590 $^{o}$C. Therefore, this desulfurization sorbent has great promise for a wide range of applications.

It is expected that most of the IGCC systems in the future would use either fluidized beds or transport beds in the desulfurization units. The objective of this project is to develop sorbents suitable for transport and fluid bed reactors. This work will be conducted in collaboration with researchers at Research Triangle Institute.

b) Development of sorbents for removal of pollutants with parts per billion level removal efficiencies

A large number of components in coal form corrosive and toxic compounds during gasification processes. These include sulfur compounds, alkali metals, halogens, and trace elements. The concentration of these materials should be reduced significantly to both protect the downstream components and meet with environmental emission requirements. According to the Vision 21 concepts, both the sulfur and chloride levels have to be reduced to less than 100 ppb in order to utilize gasification gas streams in fuel cell applications. Even more stringent requirements are expected if the fuel is to be utilized in chemical production applications. The objective of this project is to develop processes for removing both sulfur levels and halogen levels to the ppb range.

NETL researchers have developed a sorbent to remove hydrogen sulfide and carbonyl sulfide to ppb levels. The sorbent has shown ppb level sulfur removal efficiency during a 20-cycle test. The regeneration of this sorbent had to be maintained above 625 $^{o}$C in order to maintain the ppb level sulfur removal efficiency. The sorbent process will be modified to lower the regeneration temperatures and to obtain the best regeneration process. A multi-cycle test will be conducted with the modified process to determine the performance of the sorbent.

**3. Characterization of High Temperature Membranes Utilized in Hydrogen Separation**

The gas stream produced during coal gasification is a significant source of hydrogen that can be used either in clean power generation or as a primary chemical feedstock. It is necessary to separate hydrogen effectively from the coal gasification gas streams for these applications. High temperature inorganic membranes can potentially be used for the hydrogen separation process. Currently there are many research projects to develop such membranes. The successful performance of these membranes requires high fluxes of hydrogen through them and excellent thermal stability. The initial reaction involved in the separation process is the adsorption of hydrogen at the surface of these non-porous membranes. The adsorbed hydrogen dissociates at the surface, becomes ionized, and the ionized hydrogen then permeates through the membrane. Thus, the surface of the membrane plays an important role in determining the initial reaction, and knowledge of the surface properties will be critically important in the membrane development program. Even though the membrane tests are conducted at high temperatures, characterizations are usually performed at ambient temperatures with limited analytical techniques. The objective of this project is to use NETL’s unique high-temperature surface analysis methods to characterize the high temperature membranes and relate the performance data to the surface properties of the membranes prepared by Argonne National Lab. Characterization work on the membranes after high-pressure hydrogen tests will also be continued.

**4. Development of Sorbents for Carbon Dioxide Capture**

Pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are two of the techniques that can be utilized for separation and removal of $CO_2$ from gas streams. The objective of this work is to develop regenerable sorbents that have high selectivity, high regenerablity, and high adsorption capacity for $CO_2$. These properties are critical for the success of the PSA and TSA processes.

We are conducting collaborative research work with Sud Chemie, a catalyst company in Louisville, KY, and they have provided various zeolites and activated carbons for this work. The effect of physical characteristics, such as average pore size, pore size distribution, major cations present, and the surface area of the sorbents, on $CO_2$ adsorption will be investigated. Theoretical calculations to obtain the optimum pore diameter for best diffusion while maintaining the high surface area will be conducted in collaboration with Carnegie Mellon University. Competitive gas adsorption studies will be conducted in a fixed bed reactor with simulated gas streams representing both combustion and gasification gas streams. Chemical analysis of the materials will be conducted using atomic absorption spectroscopy, SEM/EDS, thermogravimetric analysis, and x-ray photoelectron/Auger spectroscopy.

**LONG TERM GOALS:**

Integrated gasification combined cycle (IGCC) technology is one of the more promising advanced power generation systems. IGCC systems incorporating hot/warm gas cleanup are predicted to offer significant improvements in environmental performance and overall plant efficiency over conventional pulverized coal-fired plants. It is expected that IGCC with hot/warm gas cleanup can achieve efficiencies in excess of 52 percent and can produce power at a 20 percent lower cost of electricity than conventional coal-based systems while reducing $CO_2$ emissions by as much as 35 percent. Removal of hydrogen sulfide from the coal gasification gas stream is important for both environmental reasons and to protect system components from corrosion and deterioration. Development of a suitable regenerable sorbent for the removal of hydrogen sulfide from the gasification product gas stream has been a major barrier issue for gas stream cleanup at hot/warm gas temperatures. Major challenges for the development of a regenerable sorbent have included decrepitation, spalling, and loss of reactivity. The long term goal of the in-house sorbent development program is to develop very cost effective sulfur control technologies for the IGCC program.

One of the major goals of the DOE gasification program and the Gasification Technologies Product Team at NETL is to develop pollutant control technologies to obtain near zero pollutant emissions. According to Vision 21 concepts, both the sulfur and chloride levels have to be reduced to less than 100 ppb in order to utilize gasification gas streams in fuel cell applications. Even more stringent requirements are expected if the fuel to be utilized in chemical production applications. One of the goals of the in-house sorbent development program is to develop clean up technologies to obtain near zero pollutants from the coal gasification gas streams.

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas $CO_2$. One of the major goals of the DOE/NETL program is to develop technologies that will allow us to utilize fossil fuels while reducing the emissions of greenhouse gases. Commercial $CO_2$ capture technologies (e.g., gas absorption by solutions of carbonates and alkanolamines) are very expensive and energy intensive. In addition, the loading of $CO_2$ is limited due to corrosion problems. Improved technologies for $CO_2$ capture are necessary. PSA and TSA are two potential techniques that could be applicable for removal of $CO_2$ from high pressure gas streams such as those encountered in IGCC systems. The long term goal of the in-house sorbent development program is to develop a cost effective commercial PSA and/or TSA system to separate and capture $CO_2$ from gas streams.

**SUMMARY ACCOMPLISHMENTS:**

Our research group has been successful in developing a desulfurization sorbent to remove sulfur to ppb range from gasification gas streams. Modifications to improve the performance of the sorbent have been effective. It was possible to eliminate the sulfur spikes obtained during the sulfidation (due to the presence of residual sulfur remaining during the regeneration) by incorporating a reductive regeneration step. It was also possible to obtain regeneration at 538 $^oC$ (1000 $^oF$). This is a major accomplishment in the sorbent development program, since there are no regenerable sorbents with ppb level sulfur removal efficiency available for warm/hot gas desulfurization. This work was done in collaboration with Sud Chemie.

Two proprietary zeolites from Sud Chemie showed excellent performance for $CO_2$ separation from gas streams. At 20 atm, it was possible to obtain $CO_2$ adsorption capacities of 7-8 moles of $CO_2$/kg of the sorbent, which is considerably higher than that obtained with commercial $CO_2$ capture processes. A new class of sorbents was developed at NETL that has a good $CO_2$ adsorption capacity and excellent regenerability. Process simulation work and molecular modeling work was initiated with Carnegie Mellon University.

**RESULTS:**

SORBENT DEVELOPMENT WORK

1. We evaluated various regeneration schemes at different temperatures with a modified ppb sulfur sorbent. One of the problems encountered during the initial tests was the presence of sulfur spikes at the beginning of sulfidation. The tests conducted during FY00 indicated that the reductive regeneration could eliminate all the initial sulfur spikes above the ppb level. It was possible to maintain a sulfur level in the ppb level during the entire sulfidation until the breakthrough using this new regeneration scheme as shown in Figure 1.

2. The regeneration of the sorbent was conducted at 648 $^oC$ (1200 $^oF$) during the 20-cycle test. The sorbent was modified to achieve regeneration at lower temperatures. It was possible to obtain regeneration at a lower temperature (538 $^oC$ (1000 $^oF$)) with the modified sorbent while maintaining the sulfur removal efficiency at the ppb level. Since the sulfidation was conducted at 316 $^oC$ (600 $^oF$), the process will be more efficient by having the regeneration temperatures at 538 $^oC$ (1000 $^oF$) rather than at 648 $^oC$ (1200 $^oF$).

3. A 10-cycle test with the modified ppb sulfur sorbent was successfully completed.

4. A 20-cycle sorbent test at conditions suitable for the Texaco gasification process was successfully completed. Texaco has indicated that they are interested in a warm gas cleanup sorbent that tolerates 60% steam during sulfidation. It is very difficult to find a sorbent that operates at 260 $^oC$(500 $^oF$) and tolerates 60% steam during sulfidation, since the presence of water promotes the reverse reaction in sulfidation ($ZnO+H_2S \dashrightarrow ZnS + H_2O$). Both low sulfidation temperature and high steam contents are detrimental to the sorbent performance. A NETL-developed sorbent was tested for 20-cycles at these conditions at Research Triangle Institute (RTI), and good performance was observed.

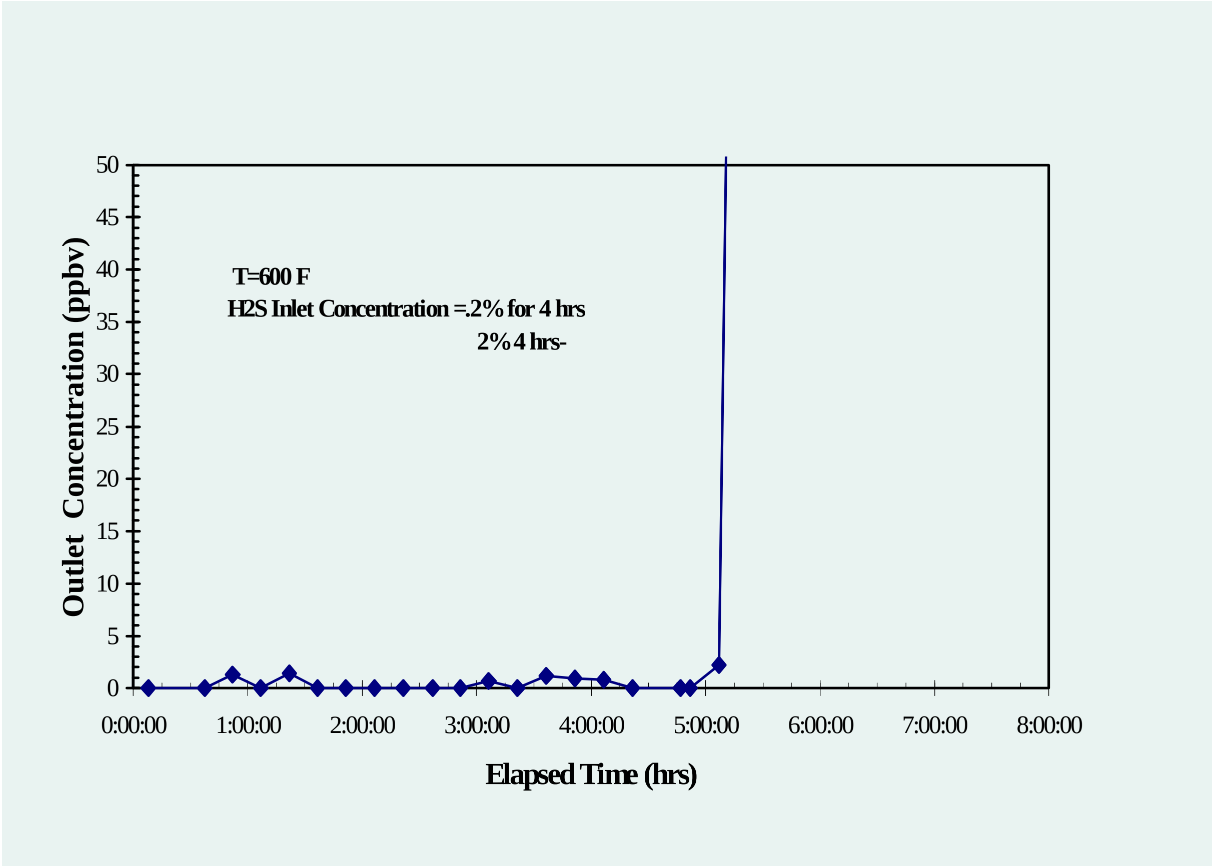


Figure1: Sulfidation of ppb sulfur sorbent after incorporation of a reductive regeneration step

DEVELOPMENT OF SORBENTS FOR CARBON DIOXIDE CAPTURE

1. The high pressure flow reactor tests were completed with zeolite 13X and activated carbon. The amount of $CO_2$ adsorbed at breakthrough (7 moles/kg) for zeolite 13X was very high and very similar to that of the equilibrium adsorption value obtained from the $CO_2$ adsorption isotherms. Activated carbon did not perform well during the high-pressure microreactor tests.

2. Volumetric adsorption/desorption isotherms of $CO_2$, $N_2$, $O_2$, and $H_2$ with two new proprietary synthetic zeolites, Z10-10 and Z10-08, from Sud Chemie were obtained. Preferential adsorption of $CO_2$ was observed with both zeolites. The $CO_2$ adsorption capacities of both zeolites were very high (6-8 moles/kg) at 300 psi. The adsorbed $CO_2$ can be fully recovered during desorption. The adsorption/desorption isotherms for Z10-08 zeolite are shown in Figure 2.

3. Volumetric gas adsorption studies on three natural zeolites were completed. The major cation in the zeolites played a significant role in the adsorption capacities. Highest adsorption capacity was observed when the major cation was sodium.

4. The effect of pore size on the sorbent performance was studied with molecular sieves 4A, 5A, and 13X. The best performance was observed with molecular sieve 13X that has a pore diameter of 1 nanometer.

5. Microreactor studies were conducted to understand the competitive adsorption of $CO_2$ from a gas mixture containing 15% $CO_2$, 82% $N_2$, and 3% $O_2$ saturated with water vapor at ambient temperature. The sorbents used in this work were molecular sieve 13X, molecular sieve 5A, activated carbon, zeolite Z10-10, zeolite Z10-08, and three natural zeolites**.** Excellent separation of $CO_2$ from gas mixtures was observed. The presence of water vapor does not seem to affect the sorbent performance. The results of the microreactor studies with Z10-08 zeolite are shown in Figure 3.

6. A new class of sorbents was prepared at NETL. These sorbents were prepared with readily available materials. The $CO_2$ adsorption capacity of the sorbent was better than that of the amine process. Consistent adsorption capacity was observed with the new sorbent during a 10-cycle test. It was possible to regenerate the sorbent at 38 $^{o}$C with nitrogen, indicating that the regenerability of the sorbent is excellent.

7. A systems analysis study of a PSA/TSA process for separation of $CO_2$ was initiated at Carnegie Mellon University. Additionally, molecular simulations of $CO_2$ adsorption on zeolites were conducted in collaboration with Carnegie Mellon University in order to understand the selective adsorption process.

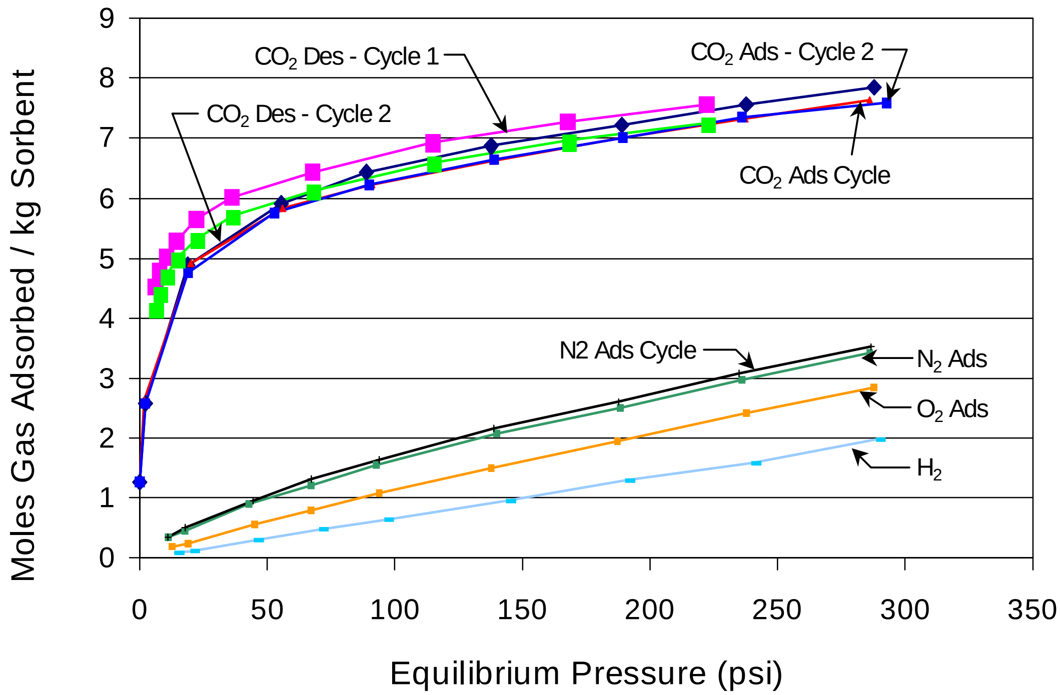
CO2 Des - Cycle 1
CO2 Ads - Cycle 2
CO2 Des - Cycle 2
CO2 Ads Cycle
N2 Ads Cycle
N2 Ads
O2 Ads
H2
Moles Gas Adsorbed / kg Sorbent
Equilibrium Pressure (psi)
0
1
2
3
4
5
6
7
8
9
0
50
100
150
200
250
300
350

Figure 2

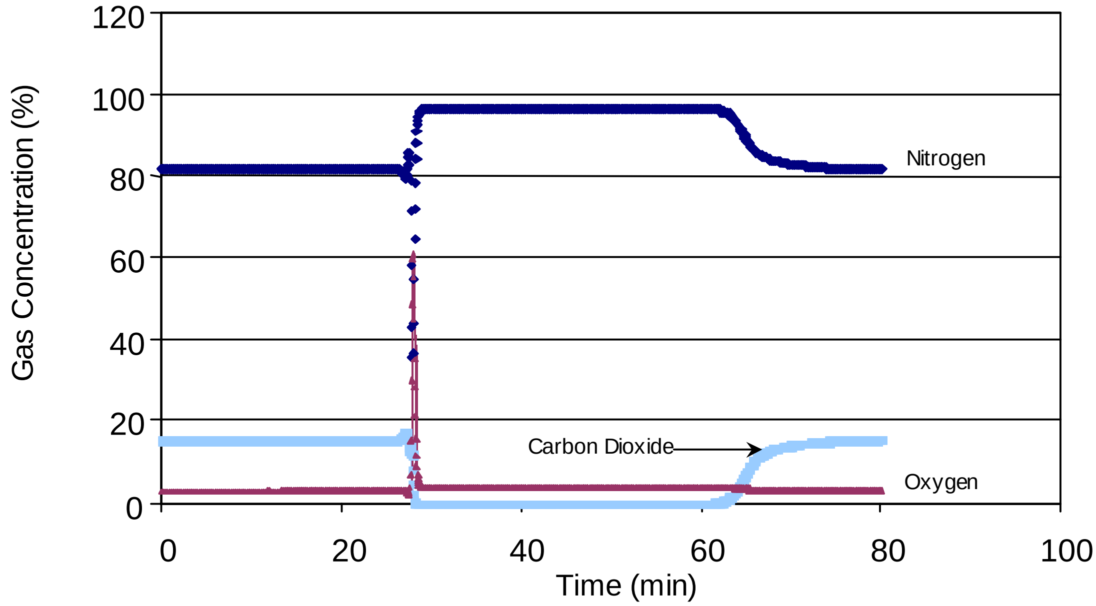


Figure 3

PATENTS AND PAPERS


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